chelate ring in the λ conformation which, in turn, fixes the adjacent sedondary amines in the *S* configuration. Since the λ conformation is fixed in both the trans and cis geometries, the trans ion has a λ chirality for the central ring and the six-membered rings have chair conformations. Thus, the assignments made using the molecular models are in complete agreement with those obtained for the spectra. Using the major rotation of the ORD curve, the complex may be labeled $(-)_{589}$-*trans*-$[Co(5(R)\text{-}Me\text{-}3,2,3\text{-}tet)Cl_2]^+$.

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Inner-Sphere Electron-Transfer Reactions of Vanadium(II) with Azidoamine Complexes of Cobalt(III)

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The rates of reduction by V^{2+} of *cis*-$Co(en)_2NH_3N_3^{2+}$, *trans*-$Co(en)_2(N_3)_2^+$, *trans*-$Co(en)_2H_2ON_3^{2+}$, and *cis*- and *trans*-$Co(NH_3)_4H_2ON_3^{2+}$ have been measured. At 25° and unit ionic strength the observed rate constants are (in M^{-1} sec^{-1}) 10.3, 26.6, 18.1, 16.6, and about 100, respectively. The respective activation parameters for the first four complexes mentioned above and for $Co(NH_3)_5Cl^{2+}$ are as follows ($\Delta H^{\ddagger}$, kcal mol^{-1}, $\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}): 12.6, −11.6; 12.2, −11.2; 11.0, −16.0; 12.1, −12.5; 7.4, −29.5. Observation of VN_3^{2+} as an unstable intermediate in the reduction of $Co(NH_3)_5N_3^{2+}$ has been made. The implications of these data on the mechanism of reduction of Co(III) complexes by V^{2+} are discussed. It is concluded that chloride is not a bridging ligand in the V^{2+} reduction of $Co(NH_3)_5Cl^{2+}$.

Introduction

The investigation of means to determine whether oxidation–reduction reactions take place by an inner-sphere or outer-sphere mechanism has been the subject of a great many studies.[1,2] There are many systems for which no direct information concerning the mechanism exists; and for those systems in which indirect arguments have been made, there are still valid doubts about the assignment of mechanism. One example of this sort will serve to illustrate the point. The rate at which a given reductant reacts with $Co(NH_3)_5N_3^{2+}$ relative to its rate with $Co(NH_3)_5NCS^{2+}$ is an often quoted means of determining mechanism.[3] For inner-sphere reactions, the former complex is reduced much more rapidly by those agents that do not have an extraordinary preference for bonding to the sulfur end of NCS^-. Upon inspection of this argument, however, it is clear that the conclusion should be that a large rate ratio implies the inner-sphere mechanism for the azide ion containing system, but no conclusion can be reached about the thiocyanate ion system: it can be either inner-sphere or outer-sphere and the large rate ratio might be found. The difficulty with this approach and most others is that the perturbing influence in the relative rate comparison is the potential bridging ligand. This study is part of a program designed to probe the question of indirect mechanism determinations by means of other types of perturbations—in this case, that of the nonbridging ligands.

The determination of the mechanism of reduction of Co(III) complexes by V(II) has been greatly aided by the observation that the rate of substitution of water on the V(II) center is slow compared to most other dipositive reductants.[4–6] Those reactions between V^{2+} and another cationic reagent that take place at rates greater than about 40 M^{-1} sec^{-1} must therefore occur by the outer-sphere mechanism.[5,7] Even though $Co(NH_3)_5Cl^{2+}$ reacts at a rate less than this limit, it has been previously suggested[8] that the mechanism of oxidation of V^{2+} by this reagent was outer sphere. This conclusion was based on the reduction of several Co(III) complexes containing chloride ion as the most likely bridging ligand that reacted faster than the limit of substitution-controlled reactivity. Nevertheless both these more rapidly reacting complexes as well as those that were less reactive followed a reactivity order as the "nonbridging" ligands[9] were changed that is very similar to the order observed for several other reductants[2,10,11] and related to them by linear free energy relationships. If $Co(NH_3)_5Cl^{2+}$ reacted by an inner-sphere path whereas, for instance, *trans*-$Co(en)_2H_2OCl^{2+}$ reacted by an outer-sphere path, it would seem likely that the *same* linear free energy relationship would not hold for both classes of reactions. The observation of Espenson[12] that the reduction of *cis*-

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[9] See footnote 3 of ref 8.

[10] R. G. Linck, *Inorg. Chem.*, **9**, 2529 (1970), and references therein.

[11] J. E. Earley, *Progr. Inorg. Chem.*, **13**, 243 (1970).

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TABLE I

ANALYTICAL DATA ON COMPLEXES

	λ_{max} (ϵ)[a]			% Co	
Complex	Lit.	Ref	Found	Calcd	Found
$[Co(NH_3)_5N_3]Cl_2$	5180 (272)	27	5170 (268)		
	5200 (265)	28			
cis-$[Co(en)_2NH_3N_3]S_2O_6$	5080 (347)	17	5060 (344)	14.79	14.65
	5110 (287)	18			
trans-$[Co(en)_2(N_3)_2]ClO_4$	5590 (326)	29	5625 (330)	. . .	. . .
	5000 (87)	22	5000 (84)		
trans-$[Co(en)_2N_3H_2O]SO_4 \cdot 2H_2O$	5000 (103)	14	5000 (101.5)	15.89	15.3
$[Co(NH_3)_4N_3H_2O]ClO_4 \cdot H_2O$	5320 (225)	25	5320 (224)[b]	14.61	15.0[b]
			5320 (221)[c]		

[a] λ in Å; ϵ in M^{-1} cm^{-1}. [b] Refers to the solid obtained as outlined in text. [c] Refers to material generated *in situ* from *cis*-$[Co(NH_3)_4(N_3)_2]ClO_4$.

$Co(en)_2(N_3)_2^+$ was accompanied by production of nonequilibrium quantities of VN_3^{2+} indicated that the azide ion system would offer an opportunity to test the assumptions involved in the above described argument. We report here the results of a study on the rate of reduction of several Co(III) complexes containing azide ion as the bridge and the implication of these results on the mechanism of the reduction of $Co(NH_3)_5Cl^{2+}$.

Experimental Section

Materials.—$[Co(NH_3)_5N_3]Cl_2$[13] and *trans*-$[Co(en)_2(N_3)_2]ClO_4$[14] were prepared by the procedures in the indicated references. $[Co(NH_3)_5Cl](ClO_4)_2$ was from the same batch as used previously.[15] Preparation of *cis*-$[Co(en)_2NH_3N_3]S_2O_6$ was achieved by addition of NaN_3 to a warm solution of *cis*-$Co(en)_2NH_3ClCl_2$,[16] followed by recrystallization with $Na_2S_2O_6$. This procedure gives a product whose spectral characteristics are in agreement with the findings of Buckingham, *et al.*,[17] but not with those of Staples.[18,19] Prior to kinetic experiments the dithionate was replaced by perchlorate with ion-exchange chromatography on a Dowex 1-X8 column. In our hands, the preparation of pure *trans*-$[Co(en)_2H_2ON_3]SO_4 \cdot 2H_2O$ from *trans*-$[Co(en)_2N_3Cl]ClO_4$[14] was extremely difficult. Because of this we outline our synthesis in some detail. We found that warming *trans*-$[Co(en)_2(N_3)_2]ClO_4$ in concentrated HCl as prescribed by Loeliger and Taube[22] led to a large quantity of purple material, *cis*-$Co(en)_2Cl_2ClO_4$,[23] that could not be satisfactorily removed from the desired blue *trans*-$Co(en)_2N_3Cl^+$. Preparation of the latter was best achieved (albeit in only about 20% yield) by stirring *trans*-$[Co(en)_2(N_3)_2]ClO_4$ with concentrated HCl for 10 min in an ice bath (*in the hood*), filtering into solid $NaClO_4$, and isolating the blue precipitate and NaCl. The crude material was extracted with cold water and reprecipitated with $NaClO_4$. Sometimes this yields pure material; for other batches, unexplainably, the extinction coefficient at 5790 Å was low, and the material was slightly greenish. Recrystallization from acetone[22] did not remove the impurity. Conversion of *trans*-$[Co(en)_2N_3Cl]ClO_4$ into the desired *trans*-azidoaquo complex was also difficult. Following the literature procedure[14] we repeatedly obtained either an oil upon addition of ethanol or a material of extinction coefficient 86–89 M^{-1} cm^{-1} at 5000 Å (based on a molecular weight of 371). Recrystallization did not affect this value. We finally managed to prepare pure *trans*-$[Co(en)_2H_2ON_3]SO_4 \cdot 2H_2O$ by dissolving the crude material in 0.2 *N* NaOH for 50 sec (a time sufficient to completely hydrolyze any residual *trans*-$Co(en)_2N_3Cl^+$ [24]), acidifying with 1 *M* H_2SO_4, and precipitating with ethanol. Two sources of the equilibrium mixture of *cis*- and *trans*-$Co(NH_3)_4H_2ON_3^{2+}$ were used. One was prepared according to the procedure of Haim[25] from *cis*-$[Co(NH_3)_4(N_3)_2]ClO_4$;[26] the other was a solid obtained by treating *cis*-$[Co(NH_3)_4(N_3)_2]ClO_4$ with 1 *M* $HClO_4$ for 15 min at 50° and precipitating brownish crystals with $NaClO_4$. Table I lists absorption and analytical data for the complexes.[27–29]

Vanadium(II) solutions were prepared and analyzed by one of two previously described procedures.[8,30] All solutions were prepared from water doubly distilled from a quartz apparatus and Baker reagent grade perchloric acid. $LiClO_4$ solutions were from previous work.[8]

Kinetic Measurements.—The course of the reactions was followed with either a Cary Model 14 or a Durrum–Gibson stopped-flow spectrophotometer. The former experiments were performed as described before, with *trans*-$Co(en)_2N_3H_2O^{2+}$ and *trans*-$Co(en)_2(N_3)_2^+$ handled by the special procedure accorded to *cis*- and *trans*-$Co(en)_2Cl_2^+$ previously.[8] Experiments with higher concentrations of V(II) were done using the thermostated stopped-flow system. Transmittance *vs.* time data were obtained from a photograph of the oscilloscope presentation. In all cases [V(II)] was sufficiently large that the reactions were pseudo first order. Plots of log $(A_t - A_\infty)$ *vs.* *t*, where *A* is the absorptivity, were linear; the rate constants were obtained from the slopes. With the exception of $Co(NH_3)_5N_3^{2+}$ the effect of laboratory light was found to be negligible; experiments in the dark were run on all compounds to confirm the values obtained under normal conditions. Experiments at $[V(II)] < 1 \times 10^{-2}$ *M* were monitored in the near-uv region, between 3000 and 3500 Å. Experiments on the stopped-flow instrument were monitored at various wavelengths depending on objective.

Results

Stoichiometry.—Spectroscopic examination of mixtures of solutions of the Co(III) complexes and V(II), with the former in excess, at wavelengths where the extinction coefficients of the Co(III) complexes, Co^{2+}, and $V(H_2O)_6^{3+}$ are known[31] allows calculation of the moles of Co(III) which reacted per mole of V(II) added. These values for the complexes studied are as follows: $Co(NH_3)_5N_3^{2+}$, 0.99; $Co(NH_3)_4N_3H_2O^{2+}$, 1.03; *trans*-$Co(en)_2(N_3)_2^+$, 0.985; *cis*-$Co(en)_2NH_3N_3^{2+}$, 0.96. (The value for *trans*-$Co(en)_2N_3H_2O^{2+}$ was not determined because under the conditions of these experiments, isomerization competes with reduction.) Thus, the overall reaction being observed can be represented by the equation $V^{2+} + CoL_5N_3^{n+} + H^+ = V^{3+} + Co^{2+} + HN_3 + 5L^{n-2+}$.

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(19) Additional evidence for purity is obtained by treating a solution of the complex in dilute $HClO_4$ with $NaNO_2$. After reaction the extinction coefficients, M^{-1} cm^{-1} (λ, Å), are 66.1 (4800), 58.4 (5070), and 47.0 (5220), literature values[20,21] are 65.2, 58.6, and 47.7 at these same wave lengths. Buckingham, *et al.*,[17] have shown this induced aquation is stereospecific.

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Kinetic Results.—For [V(II)] < 1 × 10^{-2} *M*, the reaction of V(II) with all of the Co(III) complexes studied except $Co(NH_3)_4N_3H_2O^{2+}$ followed simple second-order kinetics. This conclusion is supported by representative data in Table II. These data indicate the absence of a significant [H^+] dependency in the suspect case,[32] *trans*-$Co(en)_2(N_3)_2^+$. Our value for the rate of reduction of $Co(NH_3)_5N_3^{2+}$ is in good agreement with that reported in the literature.[28] The reduction of $Co(NH_3)_4N_3H_2O^{2+}$ was found to occur by two parallel paths at 19°; at 25°, such behavior was barely discernible in experiments on the Cary because the first path was too rapid. This behavior is consistent with $Co(NH_3)_4H_2ON_3^{2+}$ existing as two isomers, cis and trans.[25] Experiments using the stopped-flow spectrophotometer at 25° indicated that the more rapidly reacting component was the trans isomer. In four runs at 5800 Å and one at 5710 Å, the change in absorbance with time was fit by a nonlinear least-squares program to the equation $A_t - A_\infty = Qe^{-k_1t} + Pe^{-k_2t}$, where A_t is the absorbance at time *t*, A_∞ is that at the end of reaction, and *Q*, *P*, k_1, and k_2 are parameters, the first two corresponding to the total absorbance change due to species 1 and 2, respectively. The average value obtained for $Q/(Q + P)$ was 0.24 ± 0.05. From the data of Buckingham, *et al.*,[14] we estimate the relative extinction coefficients of *cis*- and *trans*-$Co(NH_3)_4H_2ON_3^{2+}$ to be 1.0 and 1.6, respectively. These data combined with Haim's value[25] for the cis to trans equilibrium constant lead to a calculated value for the absorbance due to the rapidly reacting component relative to the total absorbance change, *i.e.*, a calculated value of $Q/(Q + P)$, of 0.26. The agreement is satisfactory. The computer program also yields a value of the rate constant for the reduction of *trans*-$Co(NH_3)_4N_3H_2O^{2+}$ by V(II). These values showed considerable scatter from run to run because of the small absorbance change; the average value of five experiments was found to be 104 ± 30 M^{-1} sec^{-1}. Table III summarizes the values obtained at other temperatures and the activation parameters[33] for these complexes, as well as those for $Co(NH_3)_5Cl^{2+}$. This latter determination agrees well with that reported by Taylor, Thorneley, and Sykes,[34] $\Delta H^{\ddagger} = 7.5$ and $\Delta S^{\ddagger} = -28.8$, evaluated at a different ionic strength ($I = 2.0$ *M*).

TABLE II
KINETIC DATA FOR V(II) REDUCTION OF Co(III)-N_3 COMPLEXES (25°; I = [H^+] = 1.0 *M*)

Complex	10^5[Co(III)$_0$, *M*	10^3[V(II)]$_0$, *M*		*k*, M^{-1} sec^{-1}
cis-$Co(en)_2NH_3N_3^{2+}$	14.1	6.06		10.0
	10.4	3.12		10.1
	7.4	3.16		9.9
	5.7	1.73		11.1
			Av	10.3 ± 0.6
trans-$Co(en)_2(N_3)_2^+$	14.0	3.99		25.5
	3.9	3.16		27.8
	6.6	2.52		26.4
	2.8	2.06		27.4
	5.3	1.21		25.1
	3.3	1.07		25.8
	2.4	1.01		26.8
	5.7	1.31		26.0[a]
	17.8	1.22		27.9[a]
	14.2	0.81		24.9[a]
	19.0	0.66		28.9[a]
			Av	26.6 ± 1.3
trans-$Co(en)_2H_2ON_3^{2+}$	14.7	3.08		17.2
	9.7	2.79		17.9
	8.7	2.15		18.3
	7.0	1.72		18.3
	7.3	1.61		18.9
	1.8	1.53		18.3
	1.6	1.48		17.3
	3.4	2.11		19.8
	3.0	1.34		16.8
	3.2	0.66		18.2
			Av	18.1 ± 0.9
$Co(NH_3)_5N_3^{2+}$	4.5	1.83		12.9
	5.4	1.72		13.6
	4.2	1.31		14.1
	3.1	0.67		12.6
	2.1	0.48		13.5
			Av	13.3 ± 0.6
cis-$Co(NH_3)_4H_2ON_3^{2+}$	3.6	2.11		15.1
	1.4	1.66		15.2
	3.3	1.42		16.4
	1.0	0.34		17.9
	0.3	0.33		17.2
	163.0	72.0[b]		19.9
	91.1	47.7[c]		16.1
	127.0	31.4[d]		16.5
	149.0	26.1[e]		15.4
	305.0	14.3[f]		16.8
	62.0	11.1[g]		15.9
	60.6	9.3[h]		17.2
			Av	16.6 ± 1.3

[a] [H^+] = 0.15 *M*; I = 1.0 *M* with $LiClO_4$. [b] Stopped-flow experiment at 5710 Å; [H^+] = 0.86 *M*; I = 1.11 *M*. [c] At 5800 Å; [H^+] = 0.91 *M*, I = 1.07 *M*. [d] At 5800 Å; [H^+] = 0.94 *M*, I = 1.07 *M*. [e] At 4400 Å; [H^+] = 0.95 *M*, I = 1.07 *M*. [f] At 5500 Å; [H^+] = 0.97 *M*, I = 1.02 *M*. [g] At 5130 Å; [H^+] = 0.98 *M*, I = 1.02 *M*. [h] At 5800 Å; [H^+] = 0.98 *M*.

Intermediate Formation.—Several reductions of $Co(NH_3)_5N_3^{2+}$ were performed on the stopped-flow spectrophotometer at wavelengths 3550–3950 Å where VN_3^{2+} is known to absorb.[35] These experiments utilized high concentrations of V(II) and low [H^+] in order to determine if VN_3^{2+} was formed in nonequilibrium concentrations. This result implies that simple pseudo-first-order reduction of $Co(NH_3)_5N_3^{2+}$ does not take place but in no way obligates us to the conclusion that VN_3^{2+} is an intermediate. To establish this latter point requires that the data be analyzed in a more comprehensive manner. We chose to write a nonlinear least-squares program that minimizes the sum of the squared deviations between the observed and calculated absorbances[36] for the kinetic Scheme I.

SCHEME I

$$A \xrightarrow{k_1} B$$

$$B \xrightarrow{k_2} C$$

Such a scheme fits the data satisfactorily (the average deviation between calculated and observed points in a typical experiment is 0.0029 absorbance unit). The computer program yields values for the parameters k_1, k_2, the extinction coefficient of B, ϵ_B, and the total absorbance change. Comparison of Scheme I with a proposed inner-sphere reduction of $Co(NH_3)_5N_3^{2+}$ by V^{2+} allows us to identify k_1 with the pseudo-first-order rate constant for reduction of $Co(NH_3)_5N_3^{2+}$, k_2 with the aquation rate constant for VN_3^{2+} at the appropriate acidity, and ϵ_B with the extinction coefficient of VN_3^{2+}. Our experiments were performed at $I \cong 2$ *M*, and the rate constants must be compared with

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(32) A. Haim, *J. Amer. Chem. Soc.*, **85**, 1016 (1963).

(33) These parameters were obtained from a nonlinear least-squares computer program with points weighted according to k_{obsd}^{-2}.

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(36) The individual data points are weighted in direct proportion to the accuracy with which the observed parameter, the transmittance of the solution, is known.

TABLE III

RESULTS ON RATES OF REDUCTION AS A FUNCTION OF TEMPERATURE[a] (I = [H$^+$] = 1.0 M)

Complex	10^3[V(II)$_0$, M	n[b]	Temp, °C	k, M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal mol^{-1} deg^{-1}
cis-$Co(en)_2NH_3N_3^{2+}$	1.77–4.14	3	19.0	6.7 ± 0.2	12.6 ± 0.3	−11.6 ± 1.0
	1.34–2.20	2	32.7	18.4 ± 0.1		
cis-$Co(NH_3)_4H_2ON_3^{2+}$	1.87–3.03	3	19.3	10.8 ± 0.5	12.1 ± 0.4	−12.5 ± 1.5
	1.38–4.81	4	32.7	27.7 ± 1.3		
	1.07–2.24	4	35.0	33.2 ± 1.6		
trans-$Co(en)_2(N_3)_2^+$	2.96–3.16	3	18.0	15.7 ± 0.2	12.2 ± 0.5	−11.2 ± 1.6
	0.10–0.71	2	18.3	16.1 ± 0.9		
	2.86–2.98	2	19.0	17.2 ± 2.2		
	0.61–1.01	2	25.1	27.2 ± 0.4		
	0.80–0.99	2	29.6	40.8 ± 0.8		
	0.94–1.42	4	32.5	42.2 ± 1.8		
	0.38	1	32.7	46.6		
	0.38–0.70	2	32.9	51.1 ± 2.0		
	0.64–1.04	3	33.4	46.5 ± 0.5		
trans-$Co(en)_2H_2ON_3^{2+}$	2.69–4.43	3	19.0	12.1 ± 0.5	11.0 ± 0.5	−16.0 ± 1.5
	1.13–2.24	3	35.0	33.9 ± 1.5		
$Co(NH_3)_5Cl^{2+}$ [c]	4.04	1	19.0	6.3	7.4 ± 0.5	−29.5 ± 3.0
	2.29–2.89	2	19.3	6.2 ± 0.2		
	1.03–4.07	3	32.5	11.1 ± 1.5		

[a] Data at 25° are presented in Table II. [b] Number of experiments within the indicated range of [V(II)]. [c] Data at 25° from ref 8.

values obtained at this ionic strength. Since Expenson and Pladziewicz[35] studied the V(III)–HN_3 system at I = 1.0 M, we have repeated their experiments at the higher ionic strength. We obtain for the rate of approach to equilibrium the rate constant

$$k_{\text{obsd}} = 9 + 41[\text{H}^+] \text{ sec}^{-1} \qquad (1)$$

At the [H$^+$] of our experiments on the V^{2+} reduction of $Co(NH_3)_5N_3^{2+}$, 0.02 M, we observed k_2 = 10.5 ± 1.0 sec^{-1}, in reasonable agreement with the value of 9.8 sec^{-1} calculated from eq 1. Table IV lists the values of the extinction coefficient of B determined by our computer program in comparison to those taken from ref 35. The two types of experiments both suffer from large errors on the values of the extinction coefficient. In the case of the reaction of V^{3+} with HN_3[35] the very small equilibrium constant for formation of VN_3^{2+} makes evaluation of that equilibrium constant or, equivalently, separation of the rate of approach to equilibrium into forward and reverse rates very difficult (see Figures 3 and 5 in ref 35). Since the value of the extinction coefficient of VN_3^{2+} depends inversely on this value of the equilibrium constant, the former, of necessity, has a rather substantial error. For the accurate determination of the extinction coefficient of B from kinetic data, either the rate of disappearance of B must be substantially smaller than its rate of appearance or the extinction coefficient of B must be much larger than that of A. Neither of these cases holds for the V^{2+} reduction of Co(III)–N_3^- complexes. Comparison of the second and third columns of Table IV shows that the extinction coefficient values do overlap within 1σ. Combining these results with that of the value of k_2, we are led to the conclusion that the intermediate in the V^{2+} reduction of $Co(NH_3)_5N_3^{2+}$ is most probably VN_3^{2+}. Further, a low value of $\epsilon_{VN_3^{2+}}$ in the V^{2+} reduction of $Co(NH_3)_5N_3^{2+}$ could be caused by competitive inner-sphere and outer-sphere reductions. This would not, of course, affect the extinction coefficients calculated from equilibrium measurements.[35] If this hypothesis is accepted, about 20% of the V^{2+} reduction of $Co(NH_3)_5N_3^{2+}$ proceeds by an outer-sphere mechanism.

TABLE IV

COMPARISON OF EXTINCTION COEFFICIENT OF VN_3^{2+}

Wavelength, Å	ϵ_B,[a] M^{-1} cm^{-1}	$\epsilon_{VN_3^{2+}}$,[b] M^{-1} cm^{-1}
3550	1410 ± 230	1830 ± 260
3750	1470 ± 210	1400 ± 200
3950	640 ± 90	860 ± 120

[a] Results from least-squares analysis of Scheme I. [b] Taken from Figure 1 of ref 35, using Q = 0.0157, the average value for the two means of evaluation of Q in this reference.

(We note in passing that experiments with *cis*-$Co(en)_2(N_3)_2^+$ as the oxidant have also been performed. These experiments repeat those of Espenson[12] but at a somewhat higher ionic strength in order to increase the concentration of V^{2+}. Least-squares analysis of these data yield extinction coefficients that are in reasonable agreement with those given in the second column of Table IV, but the observed rate constant, k_2, is higher than that observed for $Co(NH_3)_5N_3^{2+}$ as the oxidant. This latter result is in agreement with that of Espenson in that he was forced to consider a V^{2+}-catalyzed path for aquation of VN_3^{2+} in order to account for the rate of aquation of VN_3^{2+} produced from the V^{2+} reduction of *cis*-$Co(en)_2(N_3)_2^+$. We do not understand this discrepancy between $Co(NH_3)_5N_3^{2+}$ and *cis*-$Co(en)_2(N_3)_2^+$ as oxidants, but attempts to investigate experimentally this question, a point remote from our purpose, were not successful. In order to see VN_3^{2+} form, high concentrations of HN_3 are necessary; if one is to ask if a V^{2+}-catalyzed path for aquation (and formation) of VN_3^{2+} is available, then V^{2+} must also be added in relatively high concentrations. However V^{2+} and HN_3 are kinetically incompatible, producing V(III), NH_4^+, and N_2,[30] the last causing bubbles to appear in the light path and render kinetic investigation spectrophotometrically difficult. One possible answer to this ambiguity has already been suggested by Espenson:[12] *cis*-$Co(en)_2(N_3)_2^+$ may be reduced by a double-bridged mechanism.)

Discussion

The reductions of the Co(III)–N_3^- complexes listed in Table III by V(II) occur with rate constants characteristic of substitution-limited inner-sphere reactions.[4,5] Our experiments using stopped-flow techniques have demonstrated that nonequilibrium concentrations of VN_3^{2+} are formed in the reduction of $Co(NH_3)_5N_3^{2+}$ and presumably are also formed in the other azide ion containing complexes listed in Table II: these V(II) reductions take place by an inner-sphere activated complex. Comparison of the activation parameters for $Co(NH_3)_5N_3^{2+}$ ($\Delta H^{\ddagger} = 11.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = -14$ cal mol^{-1} deg^{-1} [28]) and *trans*-$Co(en)_2(N_3)_2^+$ with those of the other azide-containing complexes studied herein and with data on substitution reactions of V^{2+} (with NCS^-, $\Delta H^{\ddagger} = 13.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = -7$ cal mol^{-1} deg^{-1};[37] for water exchange, $\Delta H^{\ddagger} = 16.4$ kcal mol^{-1}, $\Delta S^{\ddagger} = 5.5$ cal mol^{-1} deg^{-1} [6]) and other oxidation–reduction reactions of V^{2+} [5,7] also supports assigning a common, and hence inner-sphere, mechanism to these azide-containing complexes of Co(III).

The Co(III)–N_3^- complexes represent a series of inner-sphere reactions that illustrate how the usual nonbridging ligand effects on rate of reduction can be quenched by substitution-limited reactions of V^{2+}. This feature can be seen by comparing the relative rate of reduction of *trans*-$Co(en)_2H_2OX^{2+}$ with *cis*-$Co(en)_2NH_3X^{2+}$ by V^{2+}. If $X^- = Cl^-$, this ratio is 140;[8] but for $X^- = N_3^-$, it is only 1.75. This quenching of the nonbridging ligand effect (an effect not limited to inner-sphere reactions[2,38]) is understandable on the basis of an inner-sphere mechanism, coupled with the relative inertness of V^{2+} to substitution. A general substitution-limited electron transfer with a provision for competitive outer-sphere reduction is Scheme II

SCHEME II

$$V^{2+} + L_5CoN_3^{n+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [L_5CoNNNV]^{(n+2)+} + H_2O$$

$$[L_5CoNNNV]^{(n+2)+} \xrightarrow{k_3} VN_3^{2+} + (5L)^{(n-2)+} + Co^{2+}$$

$$V^{2+} + L_5CoN_3^{n+} \xrightarrow{k_4} V^{3+} + Co^{2+} + (5L)^{(n-2)+} + N_3^- \text{ (outer-sphere)}$$

which leads to $k_{obsd} = k_1k_3(k_2 + k_3)^{-1} + k_4$. For the limiting case of $k_3 > k_2$ and $k_1 > k_4$, the rate becomes dependent on the rate of formation of the "precursor" complex, k_1. This parameter is, apparently, not influenced strongly by nonbridging ligand perturbations (see below). Thus the substitution behavior of V^{2+} limits the rate and quenches the nonbridging ligand effect until the point is reached in which the nonbridging ligand perturbation becomes sufficient to cause a change in mechanism to outer-sphere, $k_4 > k_1$. Our limited experiments on *trans*-$Co(NH_3)_4H_2ON_3^{2+}$ ($k \cong 100$ M^{-1} sec^{-1}) suggest the above-mentioned change occurs for this complex. We believe these data demonstrate how rate-limiting water substitution affects the nonbridging ligand behavior of inner-sphere reactions. There is no evidence that the reaction of V^{2+} with Co(III)–N_3^- complexes should be nonrepresentative of other reactions in which the rate of substitution on the reductant is reached. These features support the assumption made previously in the study of the V^{2+} reduction of Co(III)–Cl^- complexes[8] and add support to the argument advanced there that the V^{2+} reductions of $Co(NH_3)_5Cl^{2+}$ and related complexes proceed by the outer-sphere mechanism, as suggested by Candlin, Halpern, and Trimm,[28,39] and not by an inner-sphere mechanism, as proposed on the basis of formal equilibrium constants for exchange reactions of transition states[40] or relative rate comparisons.[41]

Because an activation process dominated by substitution on the transition metal ion reactant would be anticipated to have different activation parameters from an electron-transfer-dominated process,[42] we measured the rate of V^{2+} reduction of $Co(NH_3)_5Cl^{2+}$ as a function of temperature. Comparison of the results is best made with *cis*-$Co(en)_2(NH_3)N_3^{2+}$, which reacts, at 25°, at nearly the same rate as $Co(NH_3)_5Cl^{2+}$. The value for $\Delta H^{\ddagger}$ for the latter complex is distinctly lower, 7.4 *vs.* 12.6 kcal mol^{-1} for *cis*-$Co(en)_2NH_3N_3^{2+}$. This difference is balanced by the less favorable ΔS^{+} for $Co(NH_3)_5Cl^{2+}$, -29.5 cal mol^{-1} deg^{-1} *vs.* -11.6 cal mol^{-1} deg^{-1} for *cis*-$Co(en)_2NH_3N_3^{2+}$. These striking differences, coupled with the nonbridging ligand argument made previously,[8] make the evidence that $Co(NH_3)_5Cl^{2+}$ reacts by an outer-sphere mechanism compelling.

It is of some interest to inquire about the underlying cause of the difference in mechanism between the V^{2+} reduction of $Co(NH_3)_5Cl^{2+}$—outer sphere—and $Co(NH_3)_5N_3^{2+}$—inner sphere. It is possible that this difference resides in greater electrostatic repulsion for the Co^{3+}–Cl^-–V^{2+} system than the Co^{3+}–NNN^-–V^{2+} system. There is some evidence that such effects may be of importance,[43] but if they are dominant, the Cr^{2+} reduction of these two complexes should show the rate for $Co(NH_3)_5N_3^{2+}$ greater than that for $Co(NH_3)_5Cl^{2+}$; the opposite is observed.[28,44] Another parameter of importance may be the electronic structure of the reductant. Table V[45-48] illustrates data on reactions whose mechanisms are known (or may be presumed as known rather confidently—Fe^{2+} [49]). The values inserted as limits for V^{2+} reflect our uncertainty about

TABLE V
THE RATE OF REDUCTION OF $Co(NH_3)_5Cl^{2+}$ AND $Co(NH_3)_5N_3^{2+}$ BY VARIOUS AGENTS[a]

Reductant	k_{Cl^-}, M^{-1} sec^{-1}	Ref	$k_{N_3^-}$, M^{-1} sec^{-1}	Ref
		A. Inner Sphere		
Cr^{2+}	2.6×10^6	44	3×10^5	28
$Co(CN)_5^{2+}$	5×10^7	45	1.6×10^6	45
Fe^{2+}	1.35×10^{-3} [b]	46	8.8×10^{-3} [b]	47
V^{2+}	≤ 3	This work	$\geq 1.33 \times 10$	22, This work
		B. Outer Sphere		
V^{2+}	7.6[b]	8	≤ 2.6	This work
$Ru(NH_3)_6^{2+}$	2.6×10^2	48	1.2	48
$Cr(bipy)_3^{2+}$	8×10^5	28	4.1×10^4	28

[a] At 25° and $I = 1.0$ M. [b] The mechanism of these reactions has not been *directly* established.

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whether an inner-sphere path competes with the dominant outer-sphere path for the oxidant $Co(NH_3)_5Cl^{2+}$, the strong indication from stopped-flow experiments that the outer-sphere path contributes less than 20% of the $Co(NH_3)_5N_3^{2+}$ oxidation of V^{2+}, and the knowledge that the electron-transfer-controlled path for $Co(NH_3)_5N_3^{2+}$ may be greater than the observed, substitution-limited rate. It can be seen from Table V that all three outer-sphere systems show the chloride ion system as the more reactive. For the four inner-sphere systems, the two in which a $\sigma(e_g)$ antibonding electron is presumably donated are more reactive with $Co(NH_3)_5Cl^{2+}$ and the two in which a $\pi(t_{2g})$ electron is presumably donated exhibit greater reactivity with $Co(NH_3)_5N_3^{2+}$. One striking difference between Cl^- and N_3^- is the presence of empty π orbitals; it may be that low-lying empty orbitals of π symmetry are necessary for efficient inner-sphere transfer of a t_{2g} electron. Stritar and Taube have discussed some systems in a similar fashion.[50,51]

Finally, some further comments on the activation data obtained in this study are warranted because of the publication of similar data on the Cr^{2+} reduction of various $Co(III)-Cl^-$ complexes.[52] These authors reported data that showed wide variations in $\Delta H^\ddagger$ as the nonbridging ligands were changed; they ascribed this behavior to a slightly more expanded version of a mechanism analogous to Scheme II (excluding the last equation), in which, it was reasoned, variations in the thermodynamics of precursor formation and in the relative magnitude of k_2 compared to k_3 would cause widely fluctuating activation parameters as the nonbridging ligands were changed. It is to be noted that the data in Table III, data on a system which presumably follows the same mechanistic scheme as does the Cr^{2+} system,[52] show little variation in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values. Further, studies on a model system[43] and on the Fe^{2+} reduction of $Co(III)-Br^-$ complexes[10] indicate little effect is to be expected from precursor stability variations in which the bridging ligand is kept constant and the nonbridging ligands are varied. In these three systems there appears to be little, if any, anomaly in the equilibrium or rate constants or activation data measured for nonbridging ligand changes in apparent contradistinction to the data on the Cr^{2+} reduction of $Co(III)-Cl^-$ complexes.

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Stereochemistry and Circular Dichroism of *trans*-Diacidobis(diamine)cobalt(III) Complexes of *N*,*N'*-Dimethylethylenediamine[1]

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The *trans*-dinitrobis(*N*,*N'*-dimethylethylenediamine)cobalt(III) and *trans*-dinitroethylenediamine(*N*,*N'*-dimethylethylenediamine)cobalt(III) ions have been prepared. Active forms arising from the asymmetric secondary amine nitrogens were resolved in each case. Pmr evidence indicates that only one *dl* pair was isolated for each complex in which the configuration about the asymmetric nitrogen centers is identical. The bis(*N*,*N'*-dimethylethylenediamine) complex gave an AA'BB' methylene multiplet. The nmr parameters are consistent with a gauche chelate ring conformation. The active dinitro complexes were converted to active *trans*-dichloro complexes with the same configurations about the nitrogen centers. The absolute configurations for both dinitro and dichloro complexes were assigned by a comparison of the sign of the CD spectra in the $A_{1g} \rightarrow T_{1g}(O_h)$ region with those for other *trans*-diacidotetramine complexes with *N*-methylamines of known configurations about the nitrogen centers. The contributions of the *N*-methyl substituent and the gauche ring to the CD intensities of the $A_{1g} \rightarrow A_{2g}(D_{4h})$ and the main component of the $A_{1g} \rightarrow E_g(D_{4h})$ bands were shown to be additive for a series of optically active *trans*-dichlorobis(diamine) complexes confirming the validity of the hexadecadal rule by S. F. Mason. A similar additivity was not found for the dinitro complexes.

Introduction

Within the past few years, Sargeson and coworkers have prepared a series of transition metal complexes containing secondary amines.[2-5] In these complexes the inertness of the coordinated nitrogen toward inversion of configuration had been demonstrated. This observation has elicited much interest in the stereochemistry of these complexes. The complexes $[Co(NH_3)_4sar]^{2+}$,[2] $[Co(NH_3)_4Meen]^{3+}$,[3] and $[Pt(en)(Meen)]^{2+}$ [5] (sar = sarcosinate anion, Meen = *N*-methylethylenediamine, en = ethylenediamine) have been resolved into mirror-image forms in which the sole source of dissymmetry is the asymmetric secondary nitrogens. Similarly, meso and racemic forms of *trans,trans*-$[Co(Meen)_2(NO_2)_2]^+$ [4] were isolated. The meso form has the two secondary nitrogens with mir-

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